

## Electronic Supplementary Information

### *Probing the fate of interstitial water in bulk bioactive glass by ab-initio simulations*

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### Computational methods

#### Glass generation

An initial array of 32SiO<sub>2</sub> 17Na<sub>2</sub>O 19CaO 2P<sub>2</sub>O<sub>5</sub> atoms was randomly arranged in a periodic cubic supercell of ~ 14 Å side, reproducing the experimental density and composition of BG45.<sup>1</sup> A partial-charge rigid-ion (RI) potential was employed in the MD generation of the glass.<sup>2</sup> Even though a shell-model potential provides a more accurate reproduction of medium-range structural features in larger samples,<sup>3</sup> the RI potentials are adequate to reproduce short-range and local structural features, and as such they have often been employed to produce the starting structure for the ab-initio refinement of relatively small models of bioglass bulk and surfaces.<sup>4, 5</sup> A different initial random configuration was used to generate each independent sample, hereafter named M1, M2, M3, M4. The random mixture was then heated up to 6000 K and a constant-temperature (NVT) MD run of 0.6 ns was performed, after which the melt was cooled down to room temperature at a 10 K/ps cooling rate. A final NVT run at 300 K completed the glass generation.

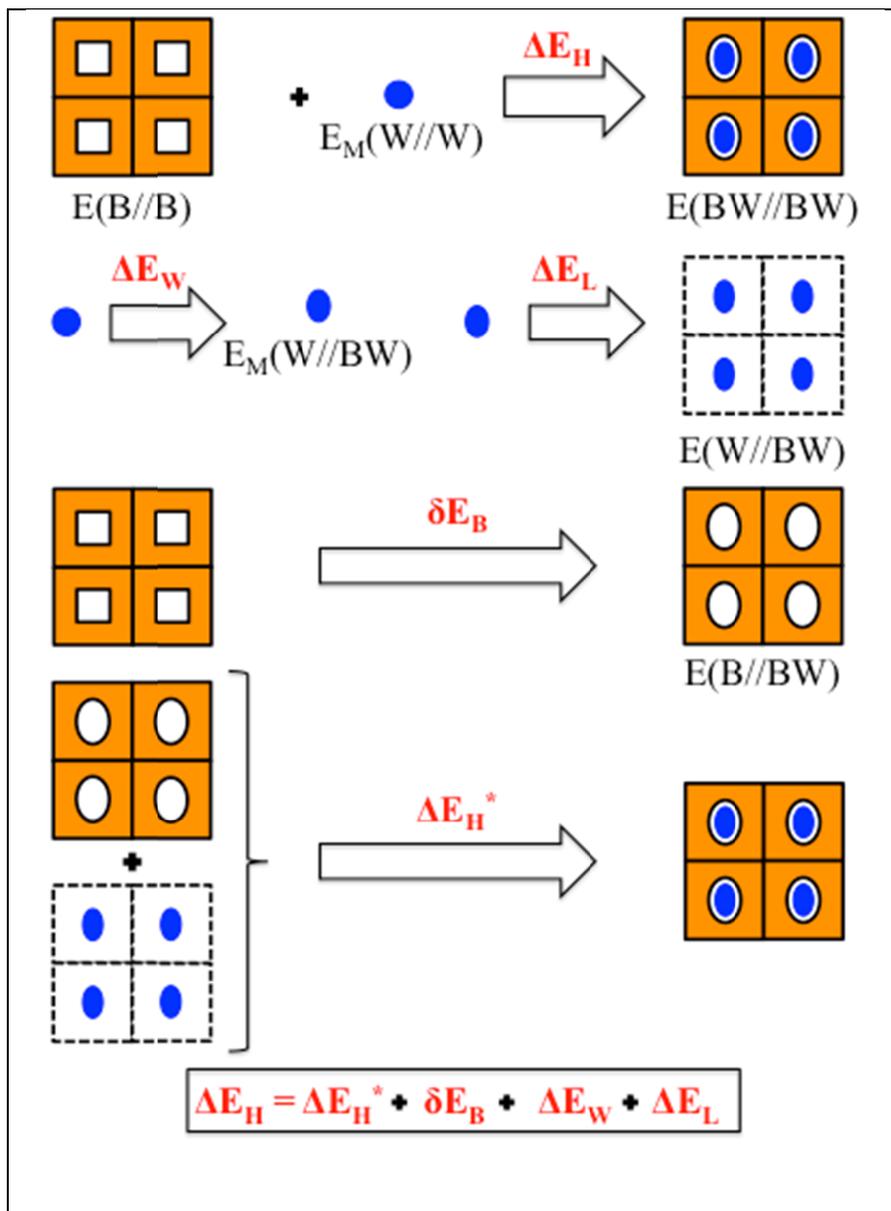
#### Car-Parrinello MD simulations

CPMD simulations were performed with the QUANTUM ESPRESSO CP code<sup>6</sup>, describing the electronic structure within the generalized gradient approximation (GGA) to density-functional theory (DFT), through the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional. Core-valence electronic interactions were represented through Vanderbilt ultrasoft pseudopotentials, with Na and Ca semicore shells included in the valence. A plane-wave basis set with cutoffs of 30 and 240 Ry was used for the smooth part of the wave functions and the augmented charge, respectively, with *k*-sampling restricted to the  $\Gamma$  point. The deuterium mass was used for hydrogen atoms, in order to effectively decouple ionic and electronic degrees of freedom while employing a larger fictitious electronic mass (700 atomic units), which in turn permits a longer MD time step (0.17 fs). The ionic temperature was controlled through a single Nosé thermostat.

## Static Optimizations

**Hamiltonian** For all the static optimizations CRYSTAL09 was used in its massively parallel implementation (MPP),<sup>7</sup> which exploits the available number of CPUs by dividing the matrix algebra operations through the pool of CPUs, ensuring a good scalability of the calculations as a function of both the system size and the number of CPUs. All the CRYSTAL09 calculations were done within the DFT, employing the Becke three parameter (B3) hybrid exchange functional in combination with the gradient-corrected correlation functional (LYP) of Lee, Yang and Parr.<sup>8,9</sup> The electronic density and its gradient are interpolated upon a pruned grid of 75 radial points and 974 angular points, divided into 5 subintervals of 86, 194, 350, 974, and 350 points (keyword XLGRID), resulting in about 4340000 grid points. In order to ensure a good accuracy in the calculation of the Fock matrix elements, the Coulomb and exchange tolerance series in periodical systems were set to 7 7 7 7 and 16. For all the calculations the Hamiltonian matrix was diagonalized only at the central point of the first Brillouin zone ( $\Gamma$  point). To lock the system in a non-conductive state, a level shifter of 0.6 Ha within the eigenvalue level-shifting technique was used.

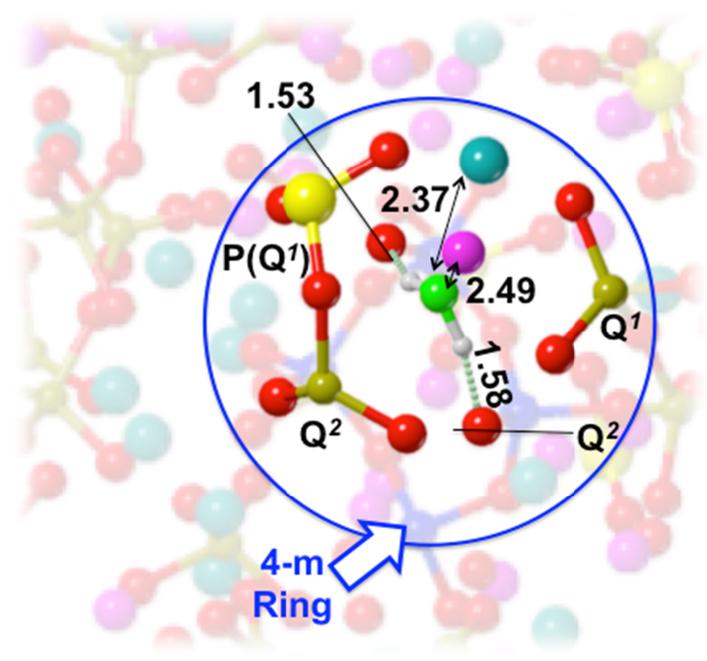
**Basis Set** The basis set adopted is an all-electron extended Gaussian-type function (GTF) basis set of split valence double- and triple- $\zeta$  quality. Na ions are described by a 8-511G basis set with the most diffuse shell exponents  $\alpha_{sp} = 0.323 \text{ bohr}^{-2}$ . Ca ions adopt a 86-511(d) basis set, with  $\alpha_{sp} = 0.295 / \alpha_d = 0.3191 \text{ bohr}^{-2}$ . Si atoms employed a 6-21G(d) modified basis ( $\alpha_{sp} = 0.13 / \alpha_d = 0.5 \text{ bohr}^{-2}$ ), whereas the P atoms were described by a 85-21G(d) basis set, with most diffuse shell exponents  $\alpha_{sp} = 0.135 / \alpha_d = 0.74583 \text{ bohr}^{-2}$ . Oxygen atoms are described with a 6-31G(d) basis set ( $\alpha_{sp} = 0.2742 / \alpha_d = 0.538 \text{ bohr}^{-2}$ ), while a 3-1G(d) basis set with  $\alpha_{sp} = 0.1613$  and  $\alpha_{pol} = 1.100 \text{ bohr}^{-2}$  for polarization was adopted for the hydrogen atoms of the water molecules.



**Scheme S1:** Graphical representation of the various terms contributing to the calculation of the hydration energy discussed in the Computational Methods section.

### Ring Hydrolysis: M1-r4\*b

The figure of the specific M1-r4\*b configuration discussed in the text (Ring Hydrolysis section) was omitted from the manuscript due to its similarity with the M1-r4\*b-MD structure shown in Figure 7a, and is reported here for reference.



**Figure S1:** Stable M1-r4\*b configuration obtained after water dissociation at ring site.

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